

# Anomalous melting behavior of solid hydrogen at high pressures

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Hydrogen is the most abundant element in the universe, and its properties under conditions of high temperature and pressure are crucial to understand the interior of large gaseous planets and other astrophysical bodies. At ultra-high pressures solid hydrogen has been predicted to transform into a quantum fluid, because of its high zero-point motion. Here we report first-principles two-phase coexistence and Z-method determinations of the melting line of solid hydrogen in a pressure range spanning from 30 to 600 GPa. Our results suggest that the melting line of solid hydrogen, as derived from classical molecular dynamics simulations, reaches a minimum of 367 K at  $\sim 430$  GPa; at higher pressures the melting line of the atomic Cs-IV phase regains a positive slope. In view of the possible importance of quantum effects in hydrogen at such low temperatures, we also determined the melting temperature of the atomic Cs-IV phase at pressures of 400, 500 and 600 GPa, employing Feynman path integral simulations. These result in a downward shift of the classical melting line by  $\sim 100$  K, and hint at a possible secondary maximum in the melting line in the region between 500 and 600 GPa, testifying to the importance of quantum effects in this system. Combined, our results imply that the stability field of the zero-temperature quantum liquid phase, if it exists at all, would only occur at higher pressures than previously thought.

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The characterization of the physico-chemical properties of hydrogen at high pressures and temperatures is of fundamental interest in physics, astrophysics, chemistry and planetary science. Previous theoretical studies [1, 2] have predicted that at sufficiently high pressures solid hydrogen would transform into a quantum liquid phase that would constitute a new state of matter, due to the fact that hydrogen has a very large zero-point energy at ultra-high pressures. Results from first-principles molecular dynamics (MD) simulations have indicated that liquid hydrogen undergoes a molecular to atomic transformation [3], which is predicted to occur at a pressure of  $125 \pm 10$  GPa along the 1500 K isotherm. Another study, employing similar techniques, has reported the finding of reentrant behavior [4] in the melting of hydrogen, i.e. the existence of a maximum along the melting line, predicted to occur at  $\sim 80$  GPa and  $\sim 900$  K, followed by a decrease of the melting temperature at higher pressures. This prediction has been subsequently confirmed by experiments [5–7], which place the maximum at  $\sim 106$  GPa and  $1050 \pm 60$  K. The occurrence of reentrant melting behavior is understood to be a necessary, though by itself not sufficient, condition for the existence of the high pressure quantum liquid phase predicted by Ashcroft [2], and thus it was taken as a strong indication of its existence by Bonev and coworkers [4]. With the assumption that the negative slope of the melting line persists to high enough pressures, it was estimated [4] that the quantum fluid state would occur at pressures close to 400 GPa. Recent

first-principles MD and quantum Monte Carlo [8] simulations have confirmed once more the reentrant behavior of the melting line, and determined a coexistence point at which both the molecular and atomic fluids coexist with the solid (phase I); this coexistence point could either be a triple point or, if the insulator-metal transition occurring in the liquid actually extends into the solid, a quadruple point.

Here we report first principles calculations of the melting temperatures of five different crystalline phases of solid hydrogen (four molecular ones and one atomic), which are the energetically most competitive phases in the pressure range 30–600 GPa. These phases are the molecular *d-hcp* (phase I), partially ordered *hcp* (*po-hcp* or phase IV), *Cmca-4*, *Cmca-12* and quasi-molecular *mC24* phases, plus the atomic *Cs-IV* phase. We have used two reliable methods (two-phase coexistence [9] and the Z-method [10]) to predict the melting curve of hydrogen in this range of pressures. Our results indicate that the high-pressure *Cs-IV* phase of hydrogen has a melting line with a positive slope. When considered together with the reentrant behavior of the melting line at lower pressures, this results in the melting line having a minimum value of 367 K at a pressure of  $\sim 432$  GPa. While the occurrence of this minimum along the melting line does not preclude the existence of the predicted quantum liquid phase [2], it would nevertheless push its stability field to higher pressures than previously thought. However, these results are based on classical simulations, and due to the lightness of hydrogen and the relatively low melting temperatures that result in this range of pressures, it is necessary to consider the possible influence of quantum effects. This is a point to which we return

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below.

The two-phase coexistence approach consists of placing within the same simulation box the solid and liquid phases directly in contact through an interface. The melting temperature is determined as that at which both phases are seen to remain stably in coexistence. At the first-principles level, such simulations are computationally demanding, as they require large cells and long simulation times, but nevertheless they are accessible with modern supercomputer facilities as recently demonstrated for the cases of Li [11] and Fe [12]. In this work we have used first principles molecular dynamics simulations based on density functional theory (DFT). For this task we employed the Vienna *ab initio* Simulation Package (VASP) [13]. Simulations were conducted in the NPH ensemble (constant number of particles,  $N$ , constant pressure,  $P$ , and constant enthalpy,  $H$ ) following the algorithm of Souza and Martins [14] as recently implemented in VASP [11, 15]. At a given external pressure, the temperature adjusts spontaneously and tends towards the coexistence temperature, as the unstable phase in the simulation is gradually consumed in favor of the stable one. By suitably repeating such simulations at various temperatures it is possible to obtain the coexistence temperature as the temperature at which both phases stably coexist and no drift in the instantaneous temperature is observed. The presence of both solid and liquid phases within the simulation box can be easily corroborated either by direct inspection or by plotting the particle density calculated at a series of planes parallel to the interface [see Fig (1)]. Crystal planes appear as spikes of high density, whereas no such spikes are present in the liquid region. The simulation was constrained to retain a tetragonal shape, with the two short sides (parallel to the plane of the interface) begin of equal length. System sizes included 980, 960 and 960 hydrogen molecules and 2048 hydrogen atoms in the  $(7 \times 7 \times 10, 2 \times 2 \times 5, 8 \times 8 \times 8, 6 \times 4 \times 10)$  simulation cells of the *d-hcp*, *po-hcp*, *Cmca-4* and Cs-IV phases, respectively. Initial configurations containing approximately equal amounts of the solid and liquid phases, plus the interface, were then generated. When both phases were found to coexist stably for a minimum of 5 ps they were assumed to be in equilibrium at the temperature and pressure conditions of the simulation. In these simulations the Brillouin zone was sampled with a grid of  $2 \times 2 \times 1$   $k$ -points; the self-consistency criterion required on the total energy was a variation smaller than  $2 \times 10^{-5}$  eV between two consecutive iterations, and the time step for integration of the equations of motion in MD was 0.5 fs.

The Z method was developed by Belonoshko and collaborators. It was first employed with empirical potentials [10], and more recently in combination with first-principles methods [16]. This method relies on the observation that, in the limit of superheating, i.e. when the solid is heated to the maximum temperature that it can sustain as a metastable phase without transform-

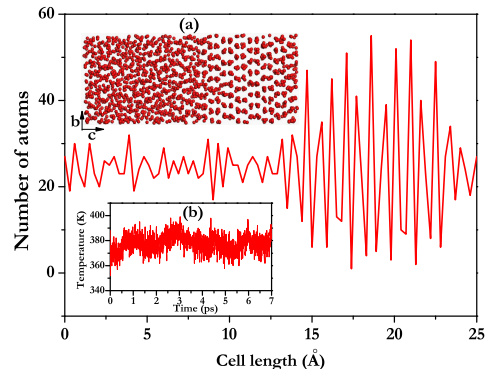


FIG. 1: (Color online) The main panel shows the particle density of the Cs-IV phase in coexistence with liquid hydrogen at 500 GPa. Regularly spaced density peaks reveal the presence of crystal planes on the right, whereas the small density oscillations around a constant value seen on the left are characteristic of the liquid phase. The upper inset, (a), shows an instantaneous configuration resulting from the same coexistence simulation. Crystal planes are clearly visible on the right side of the image, and the interface and liquid are discernible on the left. The lower inset, (b), shows the time dependence of the instantaneous temperature of the simulation shown in the main panel. The temperature has no tendency to drift, oscillating around an average value of 378 K with a standard deviation smaller than 20 K, as obtained from the last 7 ps of simulation.

ing into the liquid, its internal energy is equal to that of the liquid phase at the thermodynamic melting temperature. Thus, the problem of determining the melting temperature can be rephrased into the problem of determining the temperature of the superheating limit. Then, running a microcanonical simulation of the perfect solid at this temperature should result in the liquid phase at the equilibrium melting temperature. We have applied this technique to calculate the melting line of hydrogen using systems consisting of 48 molecules for the molecular phases (*po-hcp*, *Cmca-4*, *Cmca-12*), and 128 atoms for the atomic Cs-IV phase, employing simulation times of at least 10 ps in each case. In these simulations the Brillouin zone was sampled a  $4 \times 4 \times 4$   $k$ -point grid, and, like for the coexistence simulations, the time step used was 0.5 fs.

Our calculated melting line for the *d-hcp* structure provides a higher melting line than that predicted in previous theoretical work [4] in the range 30–200 GPa, but nevertheless in good agreement with experimental measurements [5, 6]. Moreover, we find a melting temperature for the *po-hcp* phase of 562 K at 300 GPa, which is similar to that obtained recently [8] (550 K at 290 GPa) using free energy calculations combined with quantum Monte-Carlo methods. A further test of the reliability of our results is the good agreement that we obtain between the melting temperatures derived from the coexis-

tence calculations and those resulting from the Z-method simulations (e.g. the simulated melting temperatures of Cs-IV phase at 400 GPa are 350 K and 362 K by using Z-method and two-phase coexistence, respectively).

Recently, phase IV has been found at room temperature and pressures above 220 GPa [17, 18]. This new phase has been interpreted as a mixed structure that includes two different molecular layers [19] and a partially ordered *hcp* (*po-hcp*) structure [20]. Previous theoretical studies [20] by the present authors suggest that the *Cmca*-12 structure is less stable than the *Cmca*-4 above 250 GPa, as the former has a higher zero-point energy than the latter. In view of this, we have calculated the melting line of the *po-hcp*, *Cmca*-12 and *Cmca*-4 phases in the range 200–500 GPa using the *ab initio* Z-method. While determining the melting temperature of the *Cmca*-4 and *Cmca*-12 phases at 300 and 350 GPa, we found that these phases transform into the *po-hcp* structure, which indicates that the latter structure is more stable than the other molecular structures at temperatures close to melting in this range of pressures. This result also indicates that phase *Cmca*-12 probably has no stability field in the phase diagram of hydrogen, which is in good agreement with our previous calculations [20]. Note that the melting temperature of the *po-hcp* (795 K) and *d-hcp* (815 K) structures is very similar at 200 GPa, and that the melting line of the *po-hcp* phase almost coincides with the extrapolation of that of the *d-hcp* phase. This is consistent with the recent experimental observation that the *d-hcp* structure becomes partially ordered, transforming into the *po-hcp* structure at room temperature and  $\sim 220$  GPa [17, 18].

At higher pressures hydrogen is expected to transform into an atomic phase. Our previous studies [21] have predicted the existence of a quasi-molecular *mC24* phase in the pressure range lying between the stability fields of the molecular *Cmca*-4 and the atomic *Cs*-IV phases. The *mC24* structure has two different bond lengths ( $\sim 0.86$  and  $0.9$  Å at 500 GPa) which are longer than that present in the molecular *Cmca* phase ( $0.78$  Å at 400 GPa). The *mC24* phase will dissociate into the atomic phase upon temperature increase (at  $\sim 350$  K), due to thermal fluctuations. Thus, in order to characterize the melting behavior of hydrogen at pressures in the range 350–600 GPa, we have calculated the melting temperatures of the *mC24* and *Cs*-IV phases by employing both the two-phase coexistence and Z-methods. We find that the intersection of the melting lines of the molecular and atomic phases takes place at  $\sim 432$  GPa and 367 K (see Fig. 2), and that the melting temperature of the *mC24* structure is systematically lower than that of the *Cs*-IV phase, indicating that the latter is more stable at temperatures close to melting.

The most intriguing observation to be extracted from our melting temperature calculations is that the phase diagram of hydrogen should have a second extremum along the melting line. The first extremum is the maximum originally reported by Bonev and coworkers [4]

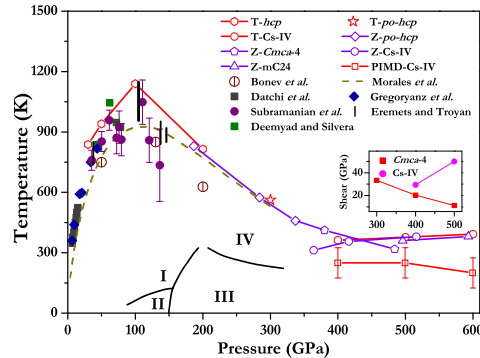


FIG. 2: (Color online) Phase diagram of hydrogen. The red and violet lines indicate the melting line obtained from our two-phase coexistence and Z-method simulations, where T and Z mean two-phase coexistence and Z-method, respectively. The solid symbols are melting data as obtained from previous experimental work [6, 7, 23, 24]. Theoretical melting data from refs. [4, 8] is represented by open symbols. The boundaries between phases I-II-III-IV at low temperatures are taken from refs. [25–28]. Inset shows the calculated shear modulus of *Cmca*-4 and *Cs*-IV structures as a function of pressure at 300K.

and later confirmed by experimental measurements [5–7]. The second extremum we find here occurs at the intersection of the melting lines of the molecular and atomic phases ( $\sim 432$  GPa, 367 K, see Fig. 2) and is a minimum, rather than a maximum. Although the molecular phase has a melting line with a negative slope at pressures above  $\sim 100$  GPa, we find the atomic *Cs*-IV phase to have a melting line with a shallow, but nevertheless positive slope above 360 GPa. Therefore, the intersection of these two melting lines occurs at a minimum. Thus it is seen that the melting behaviors of the molecular and atomic phases are qualitatively different. In order to further assert this difference in melting behavior, we have calculated the finite temperature shear modulus of the *Cmca*-4 and *Cs*-IV phases at 300 K at pressures between 300 and 500 GPa. According to the Born melting criterion [22], melting occurs when the temperature is such that the shear modulus of the solid phase reduces to zero. Thus we expect to observe a strong correlation between the behavior of the shear modulus and that of the melting temperature as a function of pressure. The finite temperature shear modulus was calculated by performing *ab initio* MD simulations of suitably deformed supercells of each phase containing 96 (in the case of the *Cmca*-4 structure) or 128 atoms (for the *Cs*-IV structure). Each run consisted of a total of 4000 steps with a time step of 0.5 fs, and the stress components were averaged over the last 2000 steps. In the case of the *Cmca*-4 phase we also run the simulation at 400 GPa for a total of 8000 time steps, but the averaged stress components were identi-

cal to those obtained in the shorter run. The calculated shear moduli for these phases at 300 K are shown in the inset of Fig. 2, where it can be seen that the moduli of the molecular phases decrease with increasing pressure, in consonance with the behavior of their corresponding melting lines. The shear modulus of the *Cs*-IV atomic phase, in contrast, displays the opposite trend, which is again in accordance with its melting behavior.

Up to this point all our results have been based on classical simulations. However, hydrogen being the lightest of elements, and the fact that the melting temperatures predicted at high pressures are relatively low, make it necessary to consider the possible influence of quantum effects on the melting temperature. To address this issue in the particular case of the *Cs*-IV atomic phase, we have employed path integral simulations [29] combined with the hysteresis method [30] to determine the melting temperature. The hysteresis method, similar in spirit to the Z-method discussed earlier, has been shown to be capable of producing accurate estimations of the melting temperature [30, 31]. We employed this method with a 72-atom super-cell of the *Cs*-IV structure with 8 beads in the quantum ring polymer (doubling the number of beads to 16 did not affect the resulting melting temperature at 400 GPa), and using  $5 \times 5 \times 3$  *k*-points for each bead. The resulting melting temperature at 400 GPa is  $\sim 250$  K, which is lower than the temperature obtained from classical molecular dynamics (350 K), confirming the importance of quantum effects in this system. Furthermore, it can be seen in Fig. (2) that the melting line including quantum effects for the *Cs*-IV is nearly flat in the range 400-500 GPa, but seems to regain a negative slope above 500 GPa. This could indicate the presence of a second local maximum in the melting line of hydrogen, followed by the re-establishment of reentrant behavior at pressures in the range 500-600 GPa. The existence of a negative slope in the melting line in this range of pressures could again be taken as a possible indication of the existence of a quantum liquid phase at high pressure, but according to our results we do not expect such a phase, if it exists, to be found at pressures below 600 GPa, the maximum pressure considered in this study. In this re-

spect, we note that a very recent study [32] employing path integral simulations has reported melting temperatures of the order of 50 K from 900 GPa onwards.

In summary, we have calculated the melting line of hydrogen up to 600 GPa using first principles molecular dynamics methods, considering melting from the *d-hcp*, *po-hcp*, *Cmca*-4, *Cmca*-12 molecular phases and the *Cs*-IV atomic phase. The obtained classical melting line of molecular hydrogen is in good agreement with previous experimental and theoretical results. We predict, however, that the melting line reaches a minimum at a pressure of  $\sim 432$  GPa, coinciding with the point at which the melting lines of the *Cmca*-4 and atomic *Cs*-IV phases cross, and that the classical melting line retains a positive (though shallow) slope at least up to 600 GPa. Quantum effects incorporated approximately via Feynman path integral simulations result in a downward shift of the melting line by as much as  $\sim 100$  K, and hint at the possibility of a secondary maximum along the melting line in the region 500 to 600 GPa. These results suggest that the proposed low-temperature quantum liquid phase, if it exists at all, will not be found at pressures below 600 GPa.

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